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SURFACE-ENHANCED RAMAN SPECTROSCOPY FOR ASTROBIOLOGY EXPLORATION ON MARS

M. Namkung¹, ¹NASA Goddard Space Flight Center, Code 691, Greenbelt, MD 20771, min.namkung-1@nasa.gov and J. T. Seo², ²Advanced Center for Laser Science and Spectroscopy, Department of Physics, Hampton University, Hampton, VA 23668, jaetae.seo@hamptonu.edu

Introduction: The absence of organics on Martian surface is a subject that had been studied intensively by many authors for decades. The simplest explanation for the missing organics used to be that they are constantly delivered to the surface but intense ultraviolet photons transmitting through the thin Martian atmosphere quickly decompose these organics[1]. Recently, influenced in part by the discovery of perchlorate by Phoenix lander, new analysis and experiments were conducted and some results suggest the presence of organics at trace level in Martian regolith. In this article, we, first, briefly review the recent progress on the subject of absence/presence of organics on Martian surface to gain perspective as to what to expect. Second, we describe why Raman spectroscopy, in particular, surface-enhanced Raman spectroscopy (SERS) is potentially the best suited for astrobiology exploration of Martian surface. Finally, we present details on the SERS implementation schemes and issues.

Organics in Martian surface: The 1976 Viking mission to Mars did not detect organic molecules on the planet's surface. It was surprising since the Martian surface is constantly bombarded by meteorites delivering various organics. Searching for the reason of this missing connection had been the center of intensive effort.

It was suggested that the presence of potent oxidant in Martian regolith converts all the organic molecules to carbon dioxide at the same rate of gaining them by meteorite bombardment [2]. The authors concluded that nonvolatile salt of benzenecarboxylates, oxalates and perhaps acetates may have been formed on the surface of Mars through oxidation of meteorite-delivered organics and these are largely invisible to the analytic instruments onboard Viking lander. Salts of these organic acids are resistant to further oxidation and may be present in Martian regolith.

Recently, Shkrob et al. [3] proposed chemical processes that are largely based on the photocatalytic decarboxylation at the surface iron oxide particulates that are abundant in the Martian regolith. Reactive radical-induced oxidation and photocatalytic reaction on the oxide particles cause mineralization of the organic compounds.

Most recently, Navarro-Gonzalez et al. [4] reanalyzed the Viking results and suggested the existence of 0.1% perchlorate and 1.5 – 6.5 ppm of organic carbon at Viking landing site 1, and 0.1 % of perchlorate and

0.7 – 2.6 ppm of organic carbon at Viking landing site 2.

To summarize, non volatile products of oxidation and even some organic carbon might be present on the Martian surface. Further, some minerals might harbor organics in areas not exposed to direct sunlight. The concentration of these can be in the order of ppm.

Raman spectroscopy for astrobiology exploration on Martian surface: Raman spectroscopy offers unique advantages over other spectroscopy techniques as analytic instruments; no need of sample preparation, light and compact instrumentation, rapid data acquisition rate and reasonably straightforward data interpretation. Hence, a broad range of literature is available on the application of Raman spectroscopy to astrobiology exploration. Among those, Ellery and Williams [5] discuss various facts related to Martian environment and emphasize that evaporite deposits are the most promising site to recover Martian biota by utilizing Raman spectroscopy. Edwards et al. [6] listed three groups of organic compounds (hopanoids, sterols and steranes) to investigate the viability of these compounds as biomarkers. They found that hopanoids are very difficult to be detected in a solid phase suggesting that certain organic compounds may not be easily detected by Raman spectroscopy. Nevertheless, those related to astrobiology may be available at trace level and it is safe to implement the surface-enhanced Raman spectroscopy method that significantly amplifies Raman peaks as described in the following section.

Surface enhanced Raman spectroscopy (SERS): The surface-enhancing effect was discovered by Fleischmann et al. in 1974 who observed surprisingly strong Raman signatures from pyridine which was adsorbed on an electromechanically roughened silver electrode as described in [7]. The Raman peak amplitude enhancement factor is routinely observed to be $10^3 - 10^7$ and in a particular case a factor of 10^{14} was claimed [8]. There are three different methods to achieve surface enhancement as reviewed in the following section.

First, the most commonly implemented method uses surface-enhancing nanoparticles submerged in aqueous solution as illustrated in the following based on the work done by the current authors of this article [9]. Figure 1 displays the schematic arrangement of molecules under investigation, Rhodamine 6G (Rh6G), and gold nanoparticles used as an enhancing agent. It is to be noted that the molecules of both ends are terminated

by gold nanoparticles. Figure 2 shows the gold nanoparticles synthesized for this work. The SERS samples were prepared by mixing two components: Rh6G in ethanol at the concentration of 2.5×10^{-3} mol/L and 0.3 mL of gold nanoparticles in water.

The experimental results of SERS are shown in figure 3. The term rice indicates the shape of the synthesized gold nanoparticles. The spectra of Rh6G are clearly seen to be surface-enhanced compared to those spectra bundled in a region close to the horizontal axis. The molecular formula of Rh6G is $C_{28}H_{31}N_2O_3Cl$ and the peaks due to well known vibration modes such as C-H and C-C bonds can be quickly identified. Nevertheless, the important features to be emphasized are the six spectra labeled as Au Rice (1 - 6) W. Water was mixed with gold nanoparticles of six different seed values, hence morphologies, but none of the spectra is seen enhanced. This is because water molecules are not terminated by gold nanoparticles and enhancement did not occur. This indicates that certain molecules are SERS-active for given nanoparticles while others are SERS-inactive. Indeed, the authors conducted SERS experiments with L-alanine, bovine serum albumin and L-glut without achieving surface-enhancement.

Apparently, forming aqueous solution with molecules under investigation and spectra enhancing nanoparticles is not suitable to *in-situ* remote operation on planetary surface. Two other methods that are more viable for the purpose of exploration.

Another commonly used technique is to drop molecular samples on to the surface of a SERS substrate with pre-fabricated nanosized patterns as depicted in Figure 4. The implementation of this technique requires producing powder samples which may be a minor issue. Nevertheless, exposing SERS substrates to the potentially dusty and windy environment can contaminate the test substrates and samples.

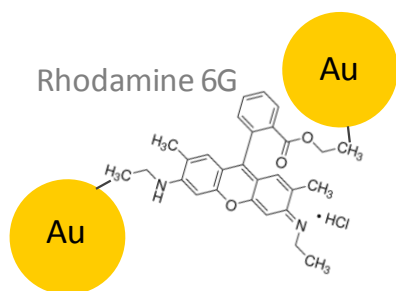


Figure 1. A schematic geometry of molecules under investigation (Rh6G in the present case) and gold nanoparticles. Notice that both ends of molecular chain are terminated by nanoparticles.

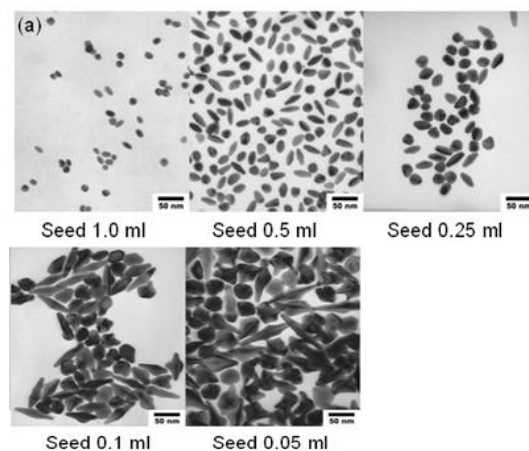


Figure 2. Gold nanoparticles synthesized for SERS experiments. Missing is the TEM micrograph for a sample with seed value of 0.025. The scale bar is 50 nm for all the five micrographs.

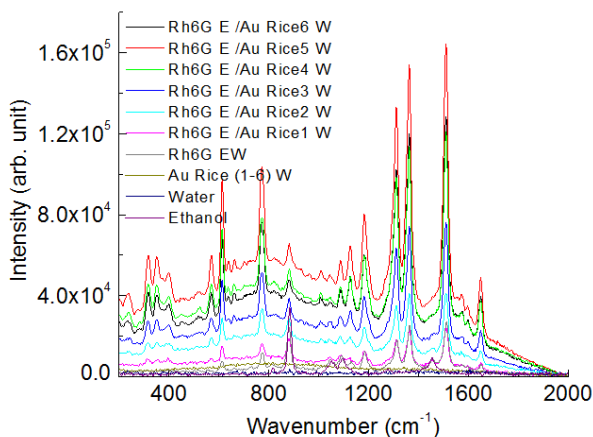


Figure 3. Surface-enhanced Raman spectra of Rh6G with gold nanoparticles of six different morphologies and more. The term “rice” refers the elliptical shape of the nanoparticles. It is seen that gold nanoparticles are unable to activate water molecules for surface-enhancement: the spectrum labeled as Au Rice (1 – 6) W clearly indicating that water is not SERS-active when gold nanoparticles used as a surface-enhancing agent.

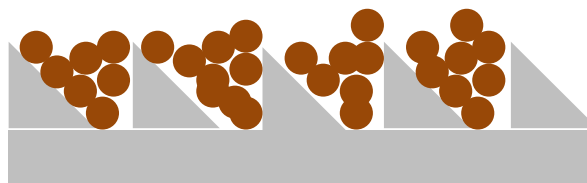


Figure 4. A schematic representation of using SERS substrate (light grey) and power samples (brown) dropped on the substrate.

The third technique is to embed the probing nanoparticles in the surface region of the target material. Ilie et al. used silver nanoparticlres as a probe detecting the extent of local transformation of carbon film [10]. Dunn et al. called this approach as the inverse SERS [11] and demonstrated that surface-enhanced Raman spectra can be obtained by first depositing small quantity of adequate agents on a ground or flat regions of rocks. Figure 5 depicts the schematics.

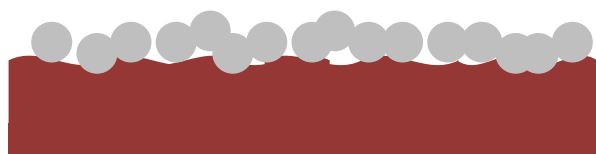


Figure 5. A SERS scheme which may be the best suited to the surface biology/chemistry assay. The local area of the ground surface is decorated with enhancing nanoparticles. This technique does not require mechanical movement of dispensing substrates and placing fine grained powered on them.

The last technique seems to be the most suitable for the implementation of SERS on Martian surface since it does not require sample collection and other mechanical movement. A device that sprays probing nanoparticles on to the soil or surface of rock may enable successful operation of SERS on Martian surface. However, as far as we are aware, there is no information related to the limitation of SERS-activeness of certain type molecules as discussed in detail for the case of SERS by aqueous solution, and further study is needed.

Conclusion: In this article, we briefly reviewed the current knowledge of organics that may be present on the surface of Mars providing some clue as to what to expect in terms of meaningful detection. We briefly discussed the well known capabilities of Raman spectroscopy applicable to astrobiology exploration on Mars. Finally, details of potential limit to the implementation of SERS are discussed.

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